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THE PRIMARY FACTORS IN PETROLEUM EMULSIONS

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The Primary Factors in Petroleum Emulsions

By

Frank Michael Tully *
B.S. (United States Naval Academy) 1942

THESIS

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THE PRIMARY FACTORS IN PETROLEUM EMULSIONS

Introduction

In order to form a stable emulsion of two immiscible or partially immiscible liquids, a third substance, an emulsifying agent, must collect at the interface, form a coherent film about the globules of the dispersed phase and thereby prevent coalescence. This is held by Dodd[1] et al. The asphaltic constituent in petroleum and its derivatives is a native emulsifying agent. Sherrick,[2] and Lottermoser and Calantar[3] emphasize the importance of asphaltic matter as the emulsifying agent. Emulsions can be broken by removing the asphaltic material by any of several means: by adsorption with fuller's earth, by extraction with alcoholic sodium hydroxide, or by precipitation by anhydrous stannic chloride. Dow and Reistle[4] found that oil recovered from emulsions had higher carbon residue values than the unemulsified portion of the same oil, which indicated that the asphaltic components had concentrated in the emulsion.

The interfacial tension between the oil and the water globules and the extent to which the emulsifying agent changes the interfacial tension are important factors in emulsibility. Lowering of the tension between the liquid phases promotes emulsification; raising of the interfacial tension

favors demulsification. Different agents have varying degrees of emulsifying power. The addition of soap to oil and water decreases the interfacial tension and increases emulsification, while such chemicals as are used to break petroleum emulsions increase the interfacial tension. The compositions of the two liquids are also important factors in emulsification, inasmuch as the interfacial tension between solvents differs and, as found by the author, a given emulsifier will have differing effect upon the interfacial tension between any two particular solvents. Hence, petroleum products, which are ordinarily mixtures of several hydrocarbons, have interfacial tensions with water dependent on their composition. That the composition of an oil affects the emulsibility of the oil was hinted by Katz and Beu,[5] "One view could be that the asphaltenes are 'potential colloids' and that solutions containing them easily convert into colloidal systems from changes in the composition of the solution." Nellensteyn[6] found that the addition of liquids, which have a surface tension below 24-26 dynes/cm. at 25° C., causes flocculation of the asphaltic micelle, while the addition of liquids having a surface tension above 26 dynes/cm. causes peptization.

Even the impurities in the water affect the interfacial tension of the system. So also does the composition of the asphaltic matter. For example, in this work it was found

that cracked asphaltic matter on a weight basis lowered the interfacial tension more than did straight-run asphaltic matter, all other factors being equal. The structure and molecular weight of the asphaltic matter, the extent to which it has been oxidized, the radical groups attached, the molecular polarity,—all influence the effect of the asphaltic matter on the interfacial tension of the system.

In any one system, however,—composed of an oil of given hydrocarbon composition, water of given impurity content, and asphaltic matter of given composition—there is a definite interfacial tension at a particular temperature. This interfacial tension is an important factor in the emulsibility of the system, i.e., the ability of the system to remain emulsified. Systems having high interfacial tensions are thermodynamically unstable, since their resolution results in a decrease of interfacial area and free energy of the system. Hence, high interfacial tension promotes coalescence of the dispersed phase and thence demulsification. Conversely, the lower the interfacial tension of the system, the more stable is the emulsion.

Primarily involved in emulsibility is the sedimentation force. There are two opposing forces acting vertically: the effective force of gravity (or centrifugal force should it be applied) and the kinetic force of diffusion. The effective force of gravity allows for the buoyancy of the oil, and for one mole of suspended particles is:

$$F_{gravity} = Ngv\Delta\rho \qquad (1)$$

where N is Avogadro's number, g is the gravitational acceleration, v is the average volume of the water particles, and $\Delta\rho$ is the difference in density between the water and oil. This force endeavors to pull the water particles to the bottom of the vessel and increase the concentration of water particles there. Opposing this force is the Brownian kinetic force which causes the colloidal particles to diffuse from a region of higher concentration to one of lower concentration, i.e., upward. The change in free energy ΔF when one mole of water particles diffuses from concentrations n_1 to n_2 is given by

$$\Delta F = RT \ln \frac{n_2}{n_1} \qquad (2)$$

The average kinetic force causing diffusion then is

$$F_{diffusion} = \frac{RT}{x_1 - x_2} \ln \frac{n_2}{n_1} \qquad (3)$$

where $x_1 - x_2$ is the distance between the points of concentration n_1 and n_2. Values of n_1 and n_2 may be determined by counting the number of particles in a given field of a microscope. The net force, or sedimentation force, at any time is therefore

$$F_{sed} = F_{grav.} - F_{diff.} \qquad (4)$$

$$= Ngv\Delta\rho - \frac{RT}{x_1 - x_2} \ln \frac{n_2}{n_1} \qquad (5)$$

When the emulsion has reached equilibrium the sedimentation force will be zero and

$$Ngv\,\Delta\rho = \frac{RT}{x_1-x_2}\ \ln\frac{n_2}{n_1}$$

$$\text{or}\quad \ln\frac{n_2}{n_1} = \frac{Ngv(x_1-x_2)\,\Delta\rho}{RT} \qquad (6)$$

Viscosity is also a factor in emulsibility. The rate of diffusion is dependent on the viscosity according to

$$D = \frac{RT}{N6\pi\eta r} \qquad (7)$$

where D is the specific rate of diffusion, η is the coefficient of viscosity of the continuous phase, and r is the radius of the spherical water particle. The greater the viscosity, the less will be the diffusion of the colloidal water particles upward, and sedimentation downward will be increased. Thus viscosity, by retarding diffusion upward, tends to decrease the emulsibility. On the other hand, water globules, which have coalesced and are of sufficient size as to be unaffected by Brownian kinetic forces and which tend to settle out under the effective force of gravity, are retarded from doing so by viscosity. According to Stokes' law this frictional force is

$$f = 6\pi\eta r \qquad (8)$$

In this instance, viscosity tends to increase the emulsibility by retarding the settling of coalesced water particles. Viscosity is a frictional force and always opposes motion, whether it be colloidal diffusion upward or the settling of coalesced globules downard. It is also significant that

the viscosity of an oil is increased by the presence of colloidal asphaltic matter, as pointed out by Lottermoser and Calantar.[3]

The asphaltic constituents of an oil are macromolecular mixtures of aromatic and naphthenic rings with paraffinic side chains.[7] Straight-run asphaltic matter is mainly composed of naphthene rings which are susceptible of dehydrogenation to aromatic rings. Under relatively severe conditions asphaltic matter may be oxidized to saponifiable products.

Solubility tests are used to divide asphaltic materials into different classes. Richardson's[8] system classifies them in their order of decreasing solubilities: maltenes, resins, asphaltenes, carbenes, and carboids. Maltenes are soluble in light petroleum naphtha (88°). Resins are a part of the maltene fraction; they are soluble in light naphtha but may be recovered from it by adsorbents such as fuller's earth. Asphaltenes are insoluble in light naphtha but soluble in benzene. Carbenes are insoluble in benzene and carbon tetrachloride but soluble in carbon disulfide. Carboids are insoluble in carbon disulfide.

Carbenes and carboids are present, if at all, in petroleum products to a very minor degree. Maltenes are soluble in the various products. Hence it is the asphaltenes and resins that constitute the bulk of the asphaltic matter which acts as

emulsifying agent. They are colloidal in size, are adsorbed at the water-oil interface, forming a unimolecular film,[9] probably aided by their polarity if they have been oxidized.

Statement of Experimental Work

The role of asphaltenes as the emulsifying agent in water-in-oil emulsions was investigated from a number of different viewpoints. The experimental work was divided into four parts:

I. A comparison was made of the abilities of cracked asphaltenes and straight-run asphaltenes as emulsifying agents in various petroleum products;

II. The emulsibilities of various petroleum products were determined before and after removal of the contained asphaltenes;

III. A study was made of the variation of the emulsibility of light petroleum products with increasing asphaltene concentration;

IV. A study was made of the variation of the interfacial tension of light petroleum products with increasing asphaltene concentration.

Part I. Comparison of cracked and straight-run asphaltenes as emulsifying agents

Procedure:

A comparison was made of the emulsifying abilities of asphaltenes contained in cracked tar and those contained in straight-run asphalt. Two fuel oils were prepared so that each had a viscosity of approximately 225 S.S.U. at 122°F. The first was a blend of 70% by volume of cracked tar cut back with 30% of straight-run gas oil; this blend will be hereinafter referred to as "the cracked blend." The second was a blend of 50% by volume of straight-run asphalt cut back with 50% of straight-run gas oil; this blend will be hereinafter referred to as "the straight-run blend." All of these products were derived from California crudes. The cracked tar had a 7.2% cyclohexane insoluble content, which was determined by the method prescribed by Abraham[10] for solubility tests. The per cent cyclohexane insoluble is an index of the amount of asphaltenes heavier than those found in straight run residua or, in other words, a measure of the severity of cracking.[11]

A few drops from a 25 milliliter dropper bottle of the cracked blend were added to a petroleum product sample, such as benzene, and a like quantity of the straight-run blend added to another equal sample of the same product.

Each mixture was shaken in a 100 milliliter graduate with equal volumes of distilled water and its resistance to separation observed. This comparison of the emulsifying effect of cracked and straight-run asphaltenes was determined in benzene, cyclohexane, carbon tetrachloride, kerosene, and straight-run gas oil.

Results:

With benzene, the straight-run asphaltenes, as contained in the straight-run blend, allowed the water to separate. A small amount of emulsion was formed below the oil layer but this, too, broke upon standing. The cracked asphaltenes caused a permanent emulsion to form.

With cyclohexane containing straight-run asphaltenes, similar results were obtained as with benzene, except that a middle layer of emulsion remained while most of the water separated. With cracked asphaltenes, a heavier emulsion was formed than in the case of benzene.

With carbon tetrachloride, the straight-run asphaltenes allowed the emulsion to break, the water going to the top; a middle layer of emulsion remained. The cracked asphaltenes caused a very thick, almost solid, emulsion to form.

With kerosene, the straight-run asphaltenes formed a better emulsion than they were capable of doing in the other products tested. As expected, however, the cracked asphaltenes formed more and thicker emulsion than did the straight-run asphaltenes.

With straight-run gas oil, the straight-run asphaltenes allowed the water to separate while the cracked asphaltenes formed a stable emulsion.

Discussion of results:

In all cases the emulsifying effect of the cracked asphaltenes was noticeably greater than that of the straight-run asphaltenes. It was noted that equal quantities of asphaltene had varying emulsifying effect on the different products tested: the composition of the oil is a factor in emulsification, but only inasmuch as it affects the more fundamental factors of interfacial tension and sedimentation force.

Part II. Emulsibility before and after removal of asphaltenes

Procedure:

The effect of asphaltene content upon the emulsibility of an oil was approached by determining the emulsibility of the oil before and after the removal of the contained asphaltenes.

The emulsibility was determined by Federal Specification Method 320.32.[12] Briefly, this test consists of paddling for five minutes 27 milliliters of the oil and 53 milliliters of distilled water in a 100 milliliter graduated cylinder. The temperature of the test was 130° F. which was obtained by immersing the graduate to the 85 milliliter mark in a water bath maintained at this temperature. The speed of rotation of the paddle was 1500 revolutions per minute, which was checked by a revolution counter. At the end of five minutes the paddle was stopped and removed from the cylinder. Readings of the demarcation between the topmost oil layer and the adjoining emulsion were taken and recorded with the time of the readings. In this work the "demulsibility" was taken as the average slope of the curve obtained by plotting the volume of the oil separated versus the time since stopping the paddle. The "emulsibility" is the numerical value of the reciprocal of the "demulsibility."

The asphaltene content of the oil was determined gravimetrically by adsorbing the asphaltenes on asbestoes. A Gooch crucible was carefully prepared by pouring into it a suspension of finely divided asbestoes fiber, sucking it dry through a suction flask, and tapping the mat tight. This process was repeated until light could just no longer be seen through the holes of the crucible. The crucible was then dried in an air oven at 105° C. for a period of two hours, after which it was allowed to cool in a desiccator. The crucible was then weighed to 0.1 milligram. The weighed crucible was placed in the suction flask and the oil filtered through it. The weight of the oil filtered was determined by weighing the stoppered flask containing the oil before and after filtering. The crucible was again placed in the air oven at 105° C., then cooled in the desiccator, and weighed. The difference in weight of the crucible before and after filtering was the weight of the adsorbed asphaltenes. The per cent asphaltene content of the oil was then calculated.

Results:

Sample data and calculations for these results are presented in the Appendix.

Sample	Asphaltene content (%)	Emulsibility with asphaltenes (min/ml)	Emulsibility without asphaltenes (min/ml)
Cracked gas oil	.035	.242	.111
Lub oil #1	.399	.568	.274
Lub oil #2	.695	.242	.120

Discussion of results:

There was a definite decrease in the emulsibility after the asphaltenes were removed. The emulsibility was lessened in each case but the final emulsibility was still characteristic of the oil. If asphaltenes were the only factor affecting emulsibility, it would be expected that their removal would reduce all oils to the same level of emulsibility. The last column shows that the final emulsibility differed in each case. In other words, the emulsibility was lessened by the removal of the asphaltenes but was still dependent on the other factors influencing interfacial tension and those affecting the sedimentation force. This is also substantiated by the fact that lub oil #2, with an asphaltene content of .695%, had a lower emulsibility than did lub oil #1, which had an asphaltene content of .399%.

Part III. Emulsibility versus asphaltene concentration

Procedure:

The emulsibilities of different light petroleum products were determined with increasing asphaltene concentration. The asphaltenes were added to such products as benzene in the form of the cracked blend (70% cracked tar and 30% straight-run gas oil). A representative sample of the cracked blend was placed in a 25 milliliter dropper bottle. To 27 milliliters of benzene in a 100 milliliter graduate was added a number of drops of cracked blend. The sample was mixed, 53 milliliters of distilled water added, and the emulsibility determined according to Federal Specification Method 320.32, outlined in the "Procedure" of Part II. The weight of the asphaltenes added was determined by weighing the dropper bottle before and after the addition of the asphaltenes to the sample. Strictly speaking, this was the weight of the cracked blend and not of the asphaltenes. But since the emulsibility was to be correlated with the relative asphaltene content, the weight of the cracked blend was considered representative of the relative asphaltene content. The emulsibilities of the same petroleum product with different amounts of asphaltene added were similarly determined.

These tests of variation of emulsibility with asphaltene concentration were made for benzene, cyclohexane, hexane, and straight-run gas oil. The tests were run both at 130° F. and 70° F. It will be noted that benzene, cyclohexane, and hexane contain six carbon atoms and are typical of the aromatics, naphthenes, and paraffins, respectively.

Results of the tests run at 130° F:

Benzene (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibilit 1/slope (min/ml)
1	.029	1.07	116	.009
2	.054	2.00	22.9	.044
2	.056	2.07	20.4	.049
3	.071	2.63	12.4	.081
3	.089	3.30	18.0	.055
4	.119	4.41	6.9	.145
4	.150	5.56	3.7	.270
5	.137	5.07	5.0	.200
6	.160	5.93	6.8	.147
8	.219	7.74	3.9	.256
8	.228	8.45	3.6	.278
10	.278	10.30	2.9	.345
12	.332	12.30	2.9	.345
15	.494	18.28	1.15	.870
15	.570	21.10	1.08	.925
15	.570	21.10	1.45	.690
20	.665	24.62	1.00	1.000
25	.805	29.80	1.10	.909

Cyclohexane (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibili 1/slope (min/ml)
1	.028	1.04	4.50	.222
2	.056	2.08	2.30	.435
2	.060	2.22	1.10	.909
3	.088	3.26	.97	1.03
3	.078	2.89	.73	1.37
5	.130	4.81	.32	3.12
5	.152	5.63	.32	3.12
8	.244	9.04	.12	8.33
10	.342	12.68	.050	20.0
15	.514	19.02	.051	19.6

Hexane (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.031	1.15	110	.0091
2	.053	1.96	107	.0093
2	.054	2.00	105	.0095
4	.110	4.07	73	.0137
5	.169	6.26	36	.028
5	.180	6.67	29	.034
10	.315	11.67	26	.038
15	.455	16.85	10.4	.096
15	.532	19.71	6.0	.167
20	.685	25.38	2.3	.435

Straight-run gas oil (130° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
0	0	0	31	.032
0	0	0	27	.037
0	0	0	33	.030
1	.003	.11	25	.040
1	.026	.96	8.7	.115
1	.028	1.04	8.7	.115
2	.051	1.89	3.2	.302
3	.082	3.04	.98	1.02
4	.108	4.00	.35	2.86
4	.117	4.34	.35	2.86
5	.152	5.63	.157	6.37
6	.169	6.26	.125	8.00
6	.180	6.67	.100	10.00
9	.281	10.41	.033	30.30

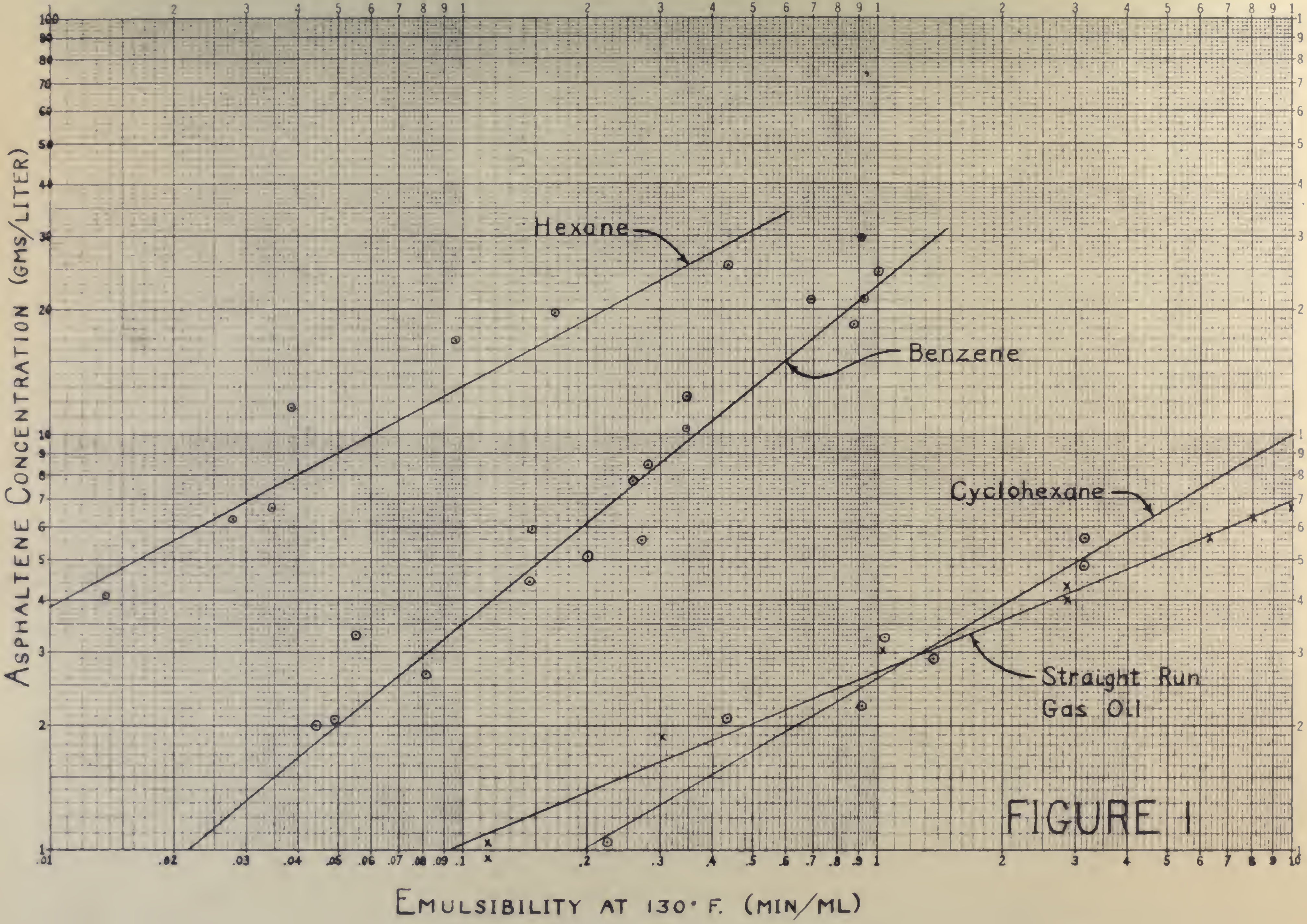


FIGURE I

Asphaltene Concentration (GMS/LITER)
Emulsibility at 130° F. (MIN/ML)
Hexane
Benzene
Cyclohexane
Straight Run Gas Oil
.01
.02
.03
.04
.05
.06
.07
.08
.09
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100

Discussion of results of tests at 130° F:

These results when plotted on log-log paper (Figure 1) yield straight lines. All curves show definitely that as the asphaltene concentration is increased, the emulsibility also increases. The explanation of the logarithmic variation of emulsibility with asphaltene concentration is had from adsorption considerations, for the asphaltenes are adsorbed at the oil-water interface and are then in a position to lower the interfacial tension, thereby increasing the emulsibility. An emulsifying agent acts by virtue of its ability to lower the interfacial tension, but before it can affect the interfacial tension it must be adsorbed in the interface. Thus emulsibility is seen to be dependent on the adsorption of the asphaltenes in the interface.

Freundlich's[13] empirical adsorption isotherm is

$$q = kc^n \qquad (9)$$

where q is the weight of material (asphaltene) adsorbed per unit area of adsorbing interface,

c is the concentration of the adsorbed material in the continuous phase (e.g. benzene), and

k and n are constants dependent on the particular system.

If the emulsibility is a linear function of the adsorption at the interface then it would follow that the emulsibility could be expressed

$$E = Kc^n \qquad (10)$$

This equation holds for the emulsibility-concentration relation of benzene, cyclohexane, hexane, and straight-run gas oil at 130^{0} F. The value of k and n are both dependent on the particular petroleum product used in the emulsification; n is the slope of the log-log plot of E versus c, and K is the value of the concentration when the emulsibility equals unity.

It should be noted that the straight-run gas oil line in Figure 1 plots very close to the cyclohexane line. It might therefore be tentatively reasoned that the straight-run gas oil was largely naphthenic.

Results of the tests run at 70° F:

Benzene (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.035	1.30	21.8	.046
3	.098	3.63	4.9	.204
8	.315	11.7	1.73	.578
10	.356	13.2	1.27	.78
10	.370	13.7	1.63	.61
20	.742	27.5	1.13	.885

Cyclohexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.026	.963	6.60	.151
2	.077	2.85	1.94	.515
3	.099	3.67	1.52	.658
6	.159	5.89	1.12	.892
7	.236	8.75	1.17	.855
7	.240	8.90	1.23	.812
8	.250	9.26	1.25	.800
10	.314	14.3	.84	1.19
15	.477	17.7	.95	1.05

Hexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Demulsibility slope (ml/min)	Emulsibility 1/slope (min/ml)
1	.029	1.07	150	.0067
4	.168	6.22	125	.0080
8	.304	11.3	117	.0085
12	.501	18.6	96	.0104
18	.666	24.7	88	.0113
24	.943	34.9	67	.0149
30	1.137	42.1	58	.0172

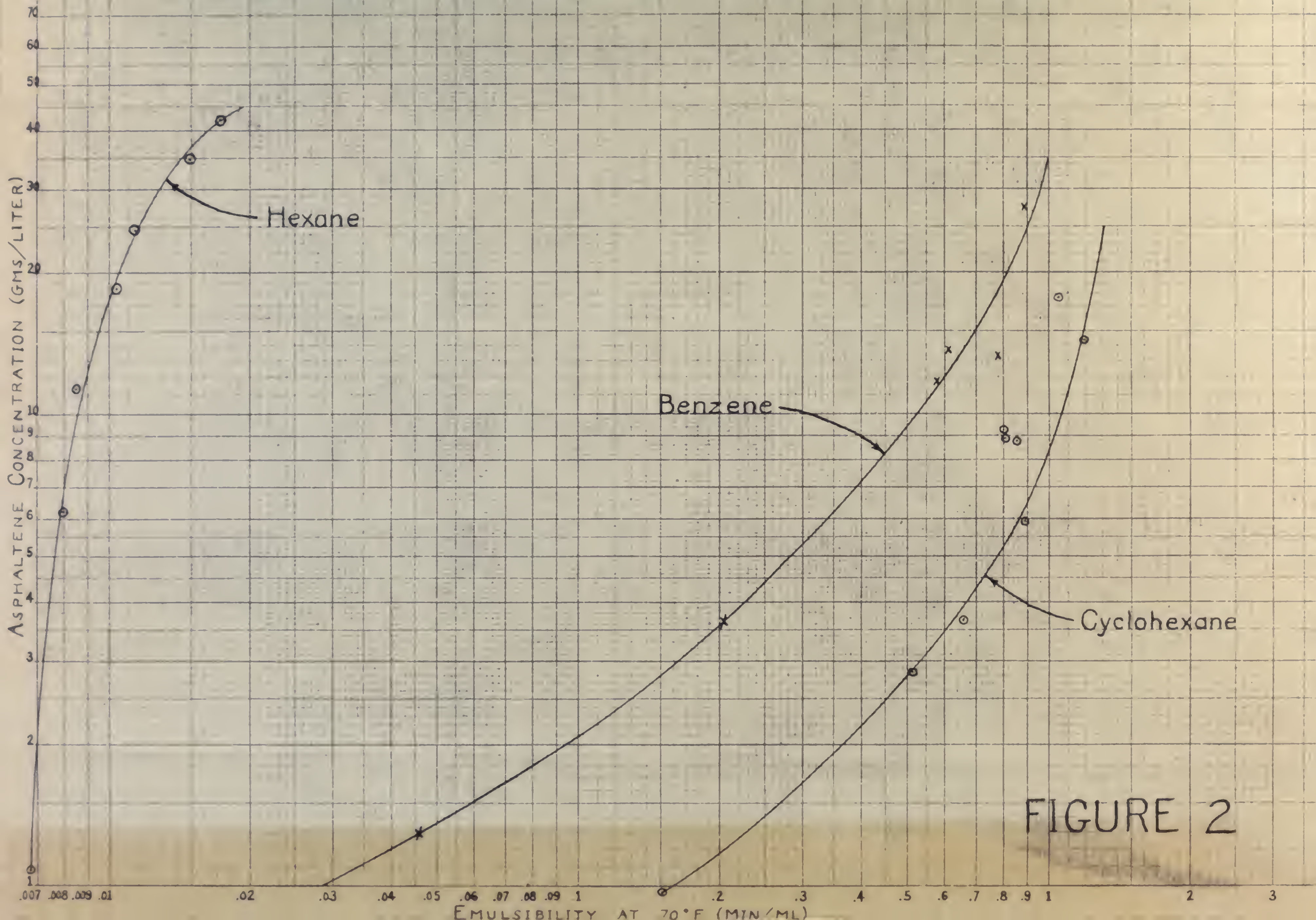

Asphaltene Concentration (Gms/Liter)
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
Hexane
Benzene
Cyclohexane
.007
.008
.009
.01
.02
.03
.04
.05
.06
.07
.08
.09
1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
Emulsibility at 70°F (min/ml)

FIGURE 2

Discussion of results of tests at 70° F:

These results for the tests run at 70° F. are plotted in Figure 2. Again is shown the increase of emulsibility with increase of asphaltene concentration. At higher concentrations the emulsibility appears to approach a maximum value asymptotically.

It should be understood that the Freundlich adsorption equation is an empirical one and, as it happens, only applies under special circumstances. An empirical equation which holds more generally was developed by Langmuir:[14]

$$w = \frac{ac}{1 + ac} \qquad (11)$$

where, applying it to the system under consideration,

w is the mass of asphaltene adsorbed per unit area of interface,

c is the concentration of the adsorbate (asphaltene) in the continous phase (e.g., cyclohexane), and

a is a constant dependent on the particular system.

Again, if the emulsibility is a linear function of the adsorption in the interface, we can express the emulsibility:

$$E = \frac{Ac}{1 + Ac} \qquad (12)$$

This relation holds better at 70° F. than does the Freundlich equation. It might be inferred that the Freundlich equation holds at raised temperatures.

Part IV. Interfacial tension versus asphaltene concentration

Procedure:

The interfacial tensions of benzene, cyclohexane, and hexane with various concentrations of asphaltene were measured. The asphaltenes, in the form of the cracked blend, were added dropwise as before from a dropper bottle, the bottle being weighed before and after addition of the asphaltene. The interfacial tension was measured by the standard drop-volume method developed by Harkins and Brown.[15] Sixty-five milliliters of the solvent being tested were mixed with a weighed amount of asphaltene in a weighing bottle. A capillary tube, whose tip had been ground and polished to a known diameter, was immersed in the solvent. Distilled water was caused to flow through the capillary and a drop of water was very gradually blown up on the immersed end of the tube. Just before the drop broke away from the tip, it was allowed to build up of itself under the pull of gravity. The volume of the drop, which was determined by burette measurements, was taken for a number of drops and the average volume computed. The interfacial tension was then calculated from the following formula:

$$\sigma = \frac{V \Delta \rho g}{2 \pi r \psi (r/V^{1/3})} \qquad (13)$$

where σ is the interfacial tension in dynes/cm,

V is the volume of the drop in cm^3,

$\Delta\rho$ is the difference in density in gm/cm^3 between the density of the water and that of the solvent mixture,

g is the gravitational constant in cm/sec^2,

r is the radius of the tip in cm,

$\psi(r/V^{1/3})$ is a correction factor obtained from the reference literature.[15]

All measurements were made at 70° F.

Results:

Sample data and calculations of the interfacial tension are presented in the Appendix.

Benzene (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm^3)	Interfacial tension (dynes/cm)	(dynes/cm)
0	0	0	.496	32.50	0
1	.031	.477	.472	31.00	1.50
4	.141	2.17	.398	26.50	6.00
8	.311	4.79	.383	25.50	7.00
15	.588	9.07	.366	24.43	8.07

Cyclohexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm^3)	Interfacial tension (dynes/cm)	(dynes/cm)
0	0	0	.368	45.20	0
1	.040	.611	.265	33.20	12.00
2	.082	1.26	.246	30.90	14.30
4	.163	2.50	.230	28.85	16.35
8	.378	5.81	.214	27.07	18.13

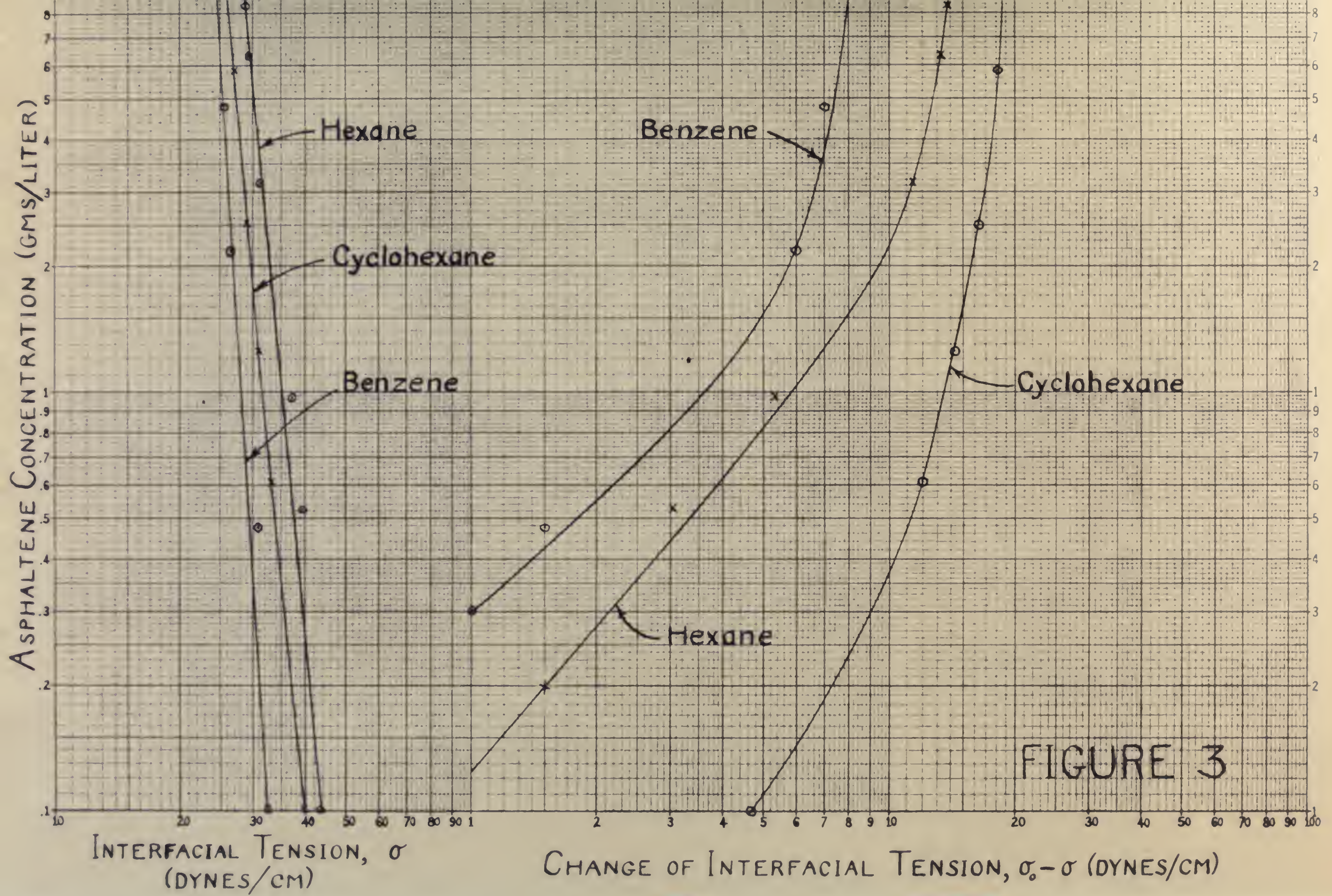


FIGURE 3

Asphaltene Concentration (gms/liter)
Interfacial Tension, σ (dynes/cm)
Change of Interfacial Tension, $\sigma_o - \sigma$ (dynes/cm)
Hexane
Cyclohexane
Benzene
Benzene
Cyclohexane
Hexane
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100

Hexane (70° F.)

No. of drops of asphaltene	Weight of asphaltene (gm)	Concentration of asphaltene (gm/liter)	Volume of drop (cm^3)	Interfacial Tension (dynes/cm)	(dynes/cm)
0	0	0	.219	42.53	0
1	.034	.523	.203	39.50	3.03
2	.063	.970	.191	37.20	5.33
6	.205	3.15	.159	31.15	11.38
12	.413	6.35	.149	29.20	13.33
16	.542	8.35	.147	28.80	13.73

Discussion of results:

In all cases the interfacial tension decreased with increase of asphaltene concentration. In Figure 3 is a log-log plot of the interfacial tension versus the asphaltene concentration. The straight lines obtained indicate that the interfacial tension is a linear function of the logarithm of the asphaltene concentration. This parallels the findings of Milner[16] who measured surface tensions. He found that when substances which strongly depress the surface tension are added to water, the surface tension is a linear function of the logarithm of the concentration of the dissolved substance for all except very dilute solutions.

In Figure 3 is also plotted the change of interfacial tension, $\sigma_0 - \sigma$, against the asphaltene concentration. It will be noted that the interfacial tension of cyclohexane is more affected by the addition of asphaltene than are the interfacial tensions of the other solvents. This would account

for the greater emulsibility of cyclohexane as indicated in Figures 1 and 2. Also favoring the emulsibility of cyclohexane is the fact that the density differential between cyclohexane and water is not excessive (ρ = .219 gm/cm^3): the less the pull of gravity, the easier it is for the diffusional force to overcome gravity and for a system to remain emulsified.

As manifest in Figure 3, the interfacial tension of hexane is more influenced by the addition of asphaltene than is the interfacial tension of benzene, although benzene is more easily emulsified than is hexane. This would seem to be a contradiction until we consider that the density differential between benzene and water (ρ = .119 gm/cm^3) is very low while that between hexane and water (ρ = .337 gm/cm^3) is very high. In other words, the light gravity of hexane is the predominant factor that makes hexane difficult to emulsify. Benzene, on the other hand, has a relatively heavy gravity and is more susceptible to emulsification by the lowering of the interfacial tension than is hexane. With cyclohexane, which has an intermediate gravity, the dominant factor is the comparatively great decrease of interfacial tension effected by the addition of asphaltene; it is this decrease of interfacial tension which makes cyclohexane more prone to emulsification than either benzene or hexane.

By entering Figures 2 and 3 with values of asphaltene concentration, corresponding values of emulsibility and interfacial tension have been obtained as follows:

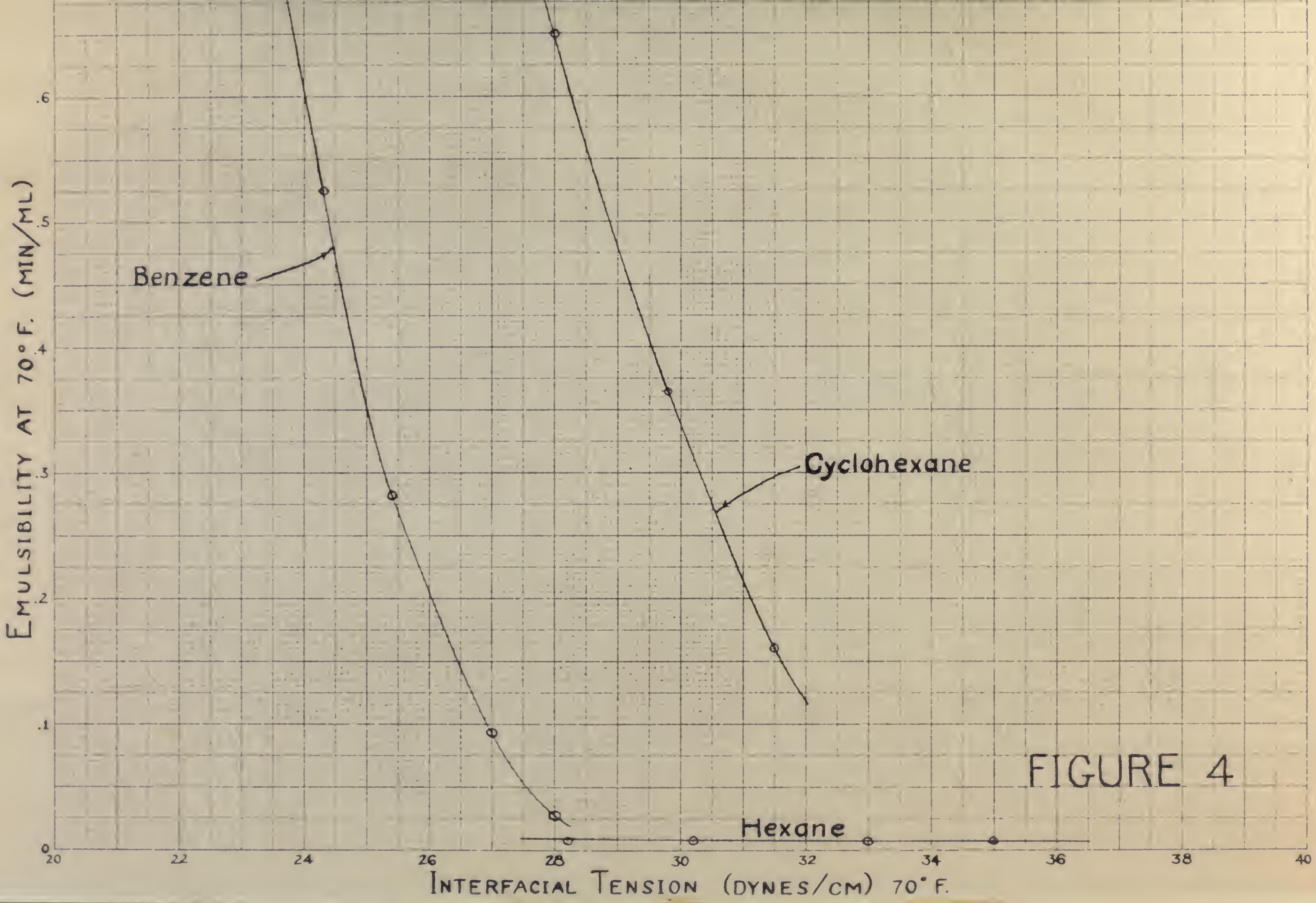

Benzene
Cyclohexane
Hexane
.6
.5
.4
.3
.2
.1
0
20
22
24
26
28
30
32
34
36
38
40
EMULSIBILITY AT 70° F. (MIN/ML)
INTERFACIAL TENSION (DYNES/CM) 70° F.

FIGURE 4

Benzene

Concentration (gm/liter)	Emulsibility (min/ml)	Interfacial tension (dynes/cm)
1.0	.029	28.0
2.0	.094	27.0
5.0	.282	25.4
10.0	.525	24.3
	Cyclohexane	
1.0	.160	31.5
2.0	.364	29.8
5.0	.775	27.3
10.0	1.06	25.9
	Hexane	
1.0	.0067	35.0
2.0	.0070	33.0
5.0	.0077	30.2
10.0	.0086	28.2

The above values of emulsibility and interfacial tension are plotted in Figure 4. It is evident from these curves that the emulsibility of benzene and cyclohexane are affected by change of interfacial tension, whereas with hexane a change of interfacial tension affects the emulsibility only slightly.

Conclusions

1. Petroleum products containing cracked asphaltenes have greater emulsibilities than those containing straight-run asphaltenes, all other things being equal.

2. The composition of the oil is a factor in emulsibility but only inasmuch as it affects the primary factors of interfacial tension and sedimentation force.

3. The emulsibility of an oil can be lessened by removal of the asphaltenes. The resultant emulsibility will still be dependent on the other factors affecting the interfacial tension and those affecting the sedimentation force.

4. The emulsibility increases with increase of asphaltene concentration: at 130° F. according to

$$E = Kc^n \qquad (10)$$

and at 70° F. according to

$$E = \frac{Ac}{1 + Ac} \qquad (12)$$

These are empirical adsorption equations. They are applicable to emulsibility because the asphaltene is adsorbed in the oil-water interface, where, by the nature of the molecule, it lowers the interfacial tension, thereby making the colloidal water particles thermodynamically more stable and less able to coalesce.

5. The interfacial tension decreases with increase of asphaltene concentration; it is a linear function of

the logarithm of the concentration except for very dilute concentrations.

6. Cyclohexane (and perhaps the naphthenes in general) is most susceptible, of the solvents tested, of emulsification by addition of asphaltenes.

7. The light gravity of hexane is the predominant factor that makes hexane difficult to emulsify.

Epilogue

The question of emulsions cannot be resolved by saying that one factor, or even two or three, are solely responsible for the formation of an emulsion. There are many factors which contribute to an emulsion, even one of the most simple type.

But we can attempt to clarify the picture by classifying these factors either as primary factors, those which directly affect the emulsibility, or as subordinate factors, those which affect the emulsibility only inasmuch as they influence the primary factors. Figure 5 is a diagrammatic sketch showing the subordination of certain factors to the primary factors.

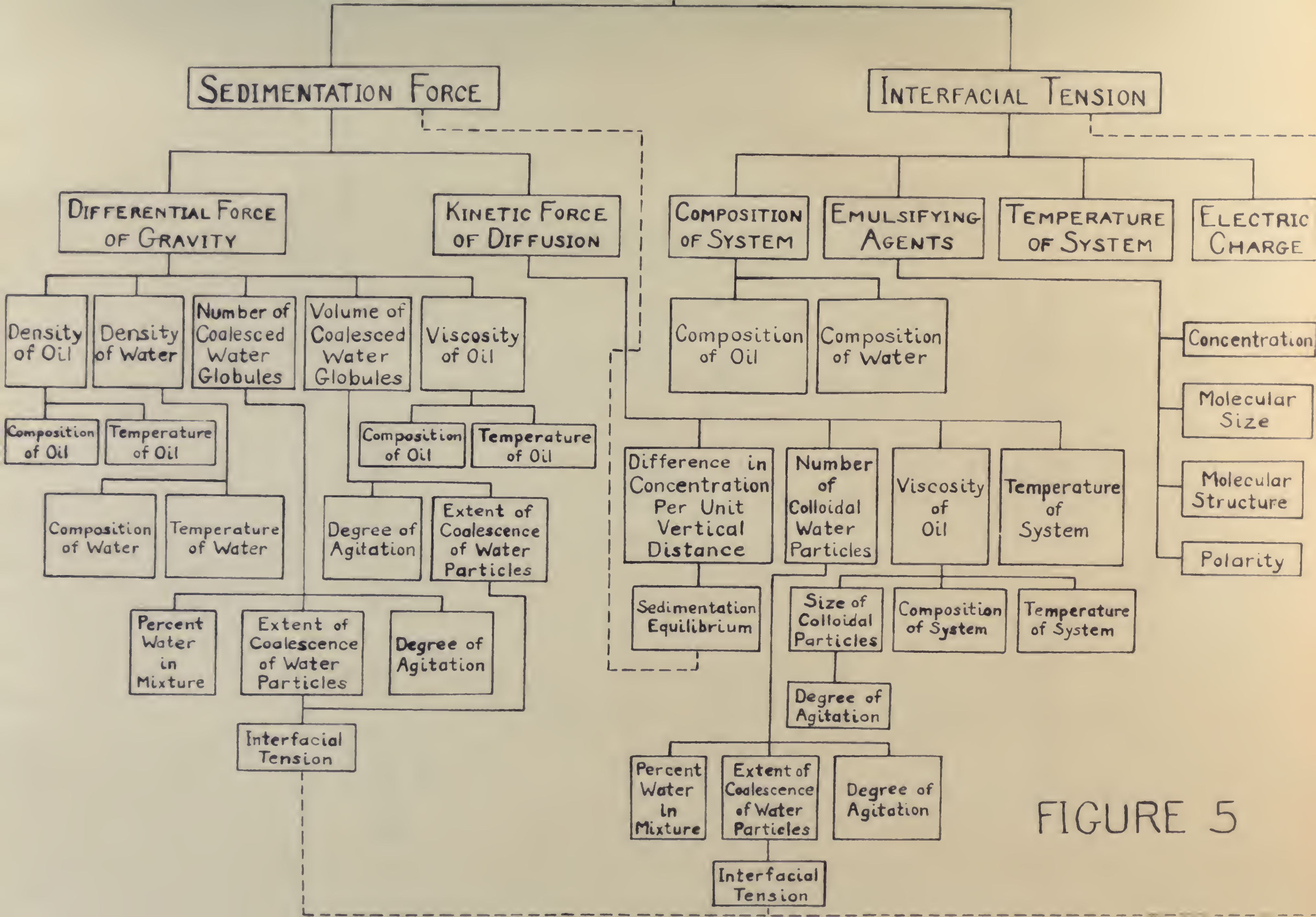

SEDIMENTATION FORCE
INTERFACIAL TENSION
DIFFERENTIAL FORCE OF GRAVITY
KINETIC FORCE OF DIFFUSION
COMPOSITION OF SYSTEM
EMULSIFYING AGENTS
TEMPERATURE OF SYSTEM
ELECTRIC CHARGE
Density of Oil
Density of Water
Number of Coalesced Water Globules
Volume of Coalesced Water Globules
Viscosity of Oil
Composition of Oil
Composition of Water
Concentration
Molecular Size
Molecular Structure
Polarity
Composition of Oil
Temperature of Oil
Composition of Oil
Temperature of Oil
Composition of Water
Temperature of Water
Degree of Agitation
Extent of Coalescence of Water Particles
Difference in Concentration Per Unit Vertical Distance
Number of Colloidal Water Particles
Viscosity of Oil
Temperature of System
Sedimentation Equilibrium
Size of Colloidal Particles
Composition of System
Temperature of System
Degree of Agitation
Percent Water in Mixture
Extent of Coalescence of Water Particles
Degree of Agitation
Interfacial Tension
Percent Water In Mixture
Extent of Coalescence of Water Particles
Degree of Agitation
Interfacial Tension

FIGURE 5

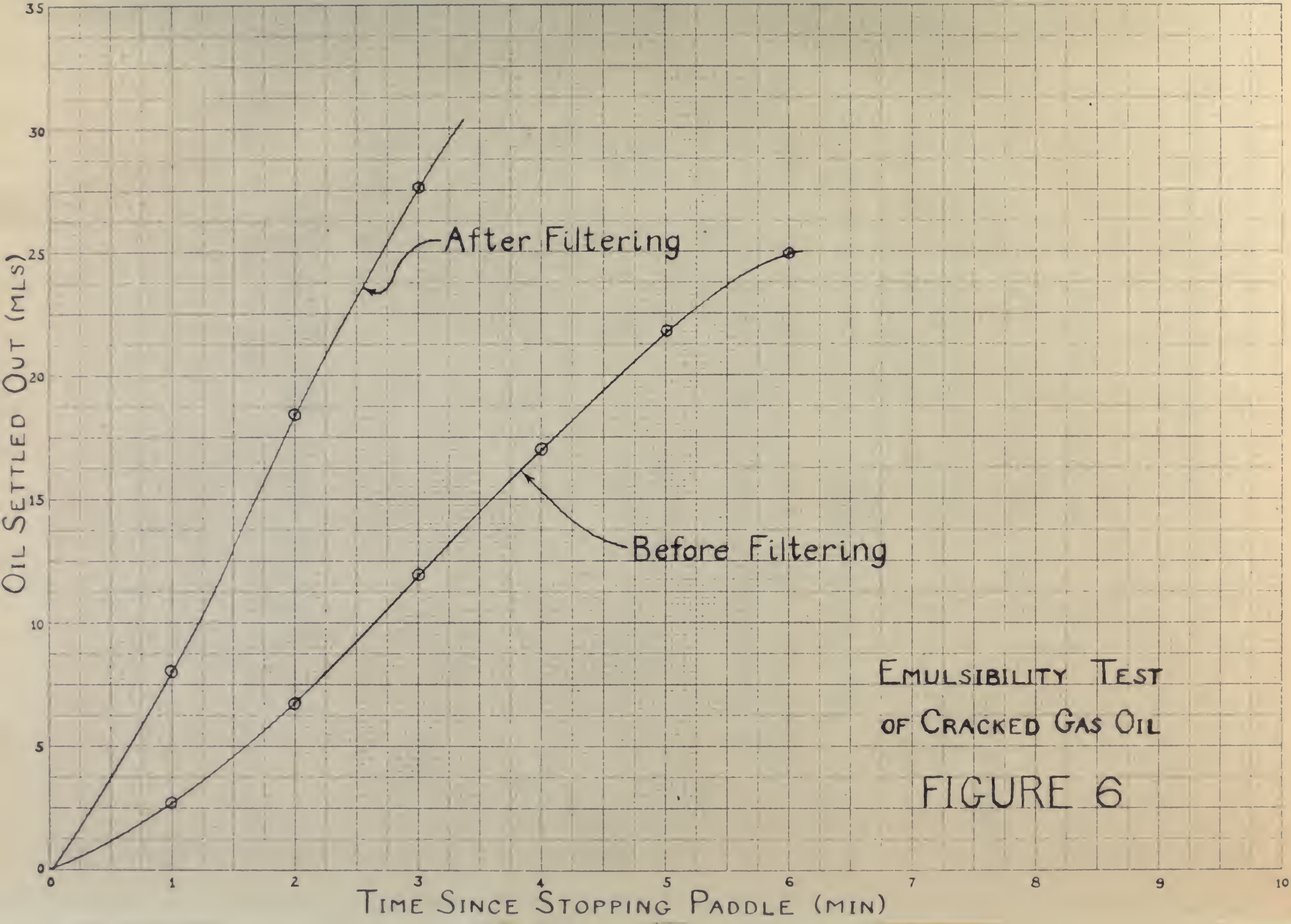
Appendix

Emulsibility test (130° F.) of cracked gas oil:

Time since stopping paddle (min)	Reading at interface between oil and emulsion	Oil settled out (mls)
	Before filtering	
0	80.7	0
1	78.0	2.7
2	74.0	6.7
3	68.8	11.9
4	63.7	17.0
5	58.9	21.8
6	55.8	24.9
	After filtering	
0	80.3	0
1	72.3	8.0
2	61.9	18.4
3	52.7	27.6

These data are plotted in Figure 6 from which is obtained:

	Before filtering	After filtering
Demulsibility (average slope)	4.12 ml/min	9.0 ml/min
Emulsibility (1/demulsibility)	.242 min/ml	.111 min/ml



Emulsibility Test of Cracked Gas Oil

FIGURE 6

Determination of per cent asphaltene content:

Weight of cracked gas oil and flask (before)	246.39 gm.
Weight of cracked gas oil and flask (after)	159.75
Weight of cracked gas oil filtered	86.64
Weight of crucible, asbestoes, and filtered asphaltenes	21.5985 gm.
Weight of crucible and asbestoes	21.5684
Weight of filtered asphaltenes	.0301

Per cent asphaltene content $= \frac{.0301}{86.64} \times 100 = .035\%$.

Calculation of interfacial tension at 70° F. between water and benzene containing 8 drops (.311 gm) of asphaltene:

Burette readings:

1.063	.862	1.249	1.260
.686	.476	.862	.878
.377	.386	.387	.382

Average volume of drop $= .383$ cm^3.

$\Delta\rho = .998 - .879 = .119$ gm/cm^3.

$g = 980$ cm/sec^2.

$r = .4475$ cm.

$r/V^{1/3} = .616$

$\psi(r/V^{1/3}) = .6225$

$$\sigma = \frac{.383 \times .119 \times 980}{2\quad .4475 \times .6225} = 25.50 \text{ dynes/cm.}$$

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